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(54) Mineral fillers

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Charges minérales

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Description

[0001] This invention relates to mineral fillers for incorporation into elastomeric compositions, to a filled elastomeric composition and to articles, particularly electric cable insulation, formed from such a filled elastomeric composition.

[0002] A mineral filler is generally introduced into an elastomeric composition intended for use as an electric insulating material in order to modify the natural elasticity of the elastomeric material so that the composition can be shaped accurately and consistently, for example by extrusion.

[0003] When an elastomeric composition is to be used to insulate a high-voltage electric cable it is important that the dissipation factor (or tangent of the loss angle, δ , by which the phase difference between applied voltage and resulting current deviates from 90°) should be as low as possible. The dielectric loss W_d in watts per metre from an insulated electric cable is given by the expression:-

$$W_d \propto 2\pi f C V^2 \tan \delta$$

where

f is the frequency of the A.C. in Hz;

C is the capacitance of the cable in farads per metre; and

V is the rated potential difference in volts between the conductor and earth.

[0004] Since the power loss is proportional to the square of the voltage, it is especially important at high voltages to keep the capacitance and the dissipation factor as low as possible.

[0005] In accordance with the invention, it has been found that the characteristics of electric cable insulation formed from an elastomeric composition containing a filler can be improved by using as the filler a kaolinitic clay which has a relatively low content of alkali metal ions. In particular, electric cable insulation incorporating such a filler has a surprisingly low dissipation factor.

[0006] Alkali metal cations may occur in a kaolinitic clay in two ways. They may be present in the crystal lattice of impurities which are associated with the kaolinitic clay. In this respect, kaolinitic clay almost always occurs in nature in association with mica, feldspar and quartz which originate from the granite matrix in which the kaolinite was formed by weathering. Both mica and feldspar contain appreciable quantities of alkali metal cations, principally potassium ions (and occasionally lithium and sodium ions) and these are generally not exchangeable or soluble in water, but are fixed relatively firmly in the crystal lattice of these impurity minerals. These impurities are very difficult to separate completely from the kaolinite and they are therefore generally present in the kaolinitic filler for end use.

[0007] Sodium ions are generally introduced into a kaolinitic clay during the processes by which the clay is beneficiated. Very rarely, potassium ions may be introduced into the clay mineral during beneficiation. Dispersing agents are generally used, and these are commonly sodium salts of polyphosphoric acids or sodium salts of homopolymers or copolymers of acrylic acid or methacrylic acid. Alkalis such as sodium hydroxide or sodium carbonate are also commonly used to correct the pH of an aqueous suspension in which the clay is treated. It may also be necessary to treat the clay with a reducing bleaching agent in order to remove staining of the clay by ferric iron compounds, and the reducing bleaching agent is often a sodium compound such as sodium dithionite or sodium bisulphite. Sodium ions, and occasionally potassium ions, which are introduced during beneficiation in these ways are generally present in an exchangeable form. "Exchangeable" cations are cations which may be removed into solution in water or may be exchanged by means of a cation exchange reaction. "Non-exchangeable" cations are those which cannot be removed into solution in water or exchanged by means of a cation exchange reaction.

[0008] The content of monovalent cations, and particularly the content of sodium ions present in a kaolinitic clay product depends also on the process by which the clay has been dewatered during its beneficiation. In some processes for producing kaolinitic clay the raw kaolinitic clay is beneficiated in suspension in water, and a large part of the water is subsequently removed by filtration and the filter cake thus formed is subjected to thermal drying to give a substantially dry product. With the water removed in the filtration step, a large proportion of the exchangeable monovalent cations is also removed, with the result that the content of exchangeable monovalent cations in the final product is generally not high. However, some kaolinitic clays which are beneficiated in suspension in water are dewatered by injecting the aqueous suspension directly in to a spray dryer, with the result that the monovalent cations remain in association with the kaolinitic clay.

[0009] In accordance with a first aspect of the present invention, there is provided an elastomeric composition including a kaolinitic clay mineral filler, characterised in that said kaolinitic clay mineral (a) is a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 ppm or (b)

is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral having a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm and a content of exchangeable alkali metal cations not exceeding 750 ppm.

[0010] In the hydrous kaolinitic clay mineral, the content of non-exchangeable alkali metal cations preferably does not exceed 7,500 ppm and the content of exchangeable alkali metal cations does not exceed 500 ppm. (The content of non-exchangeable alkali metal cations may be measured by an X-ray fluorescence technique).

[0011] Typically, in the present invention, the predominant non-exchangeable alkali metal cation present in the hydrous kaolinitic clay filler will be potassium, whilst the predominant exchangeable alkali metal cation will be sodium.

[0012] The hydrous kaolinitic clay mineral for use in the first aspect of this invention may be prepared by initially selecting a suitable clay which naturally, or after beneficiation to remove impurities containing non-exchangeable alkali metal cations, such as mica and feldspar, has a content of non-exchangeable alkali metal cations below the desired level and, secondly, treating the clay, either during beneficiation or in a separate step if necessary, such that the resultant treated clay has an exchangeable alkali metal cations content not exceeding 750 ppm. The clay mineral may then be calcined.

[0013] The hydrous kaolinitic clay mineral may be treated to reduce the number of alkali metal cations (normally sodium ions) which may, for instance, have accumulated during beneficiation, by subjecting an aqueous suspension of the beneficiated clay to mechanical filtration whereby the exchangeable alkali metal cations are removed in solution. Alternatively, or in addition, a large proportion of the exchangeable alkali metal cations present in a kaolinitic clay for use in the invention may be removed by treating the kaolinitic clay mineral to a cation exchange operation whereby monovalent exchangeable cations in the clay are removed and replaced by multivalent cations (i.e. cations having a valency of two or more).

[0014] Cation exchange reactions on clays are known *per se* and are normally conducted by placing the clay in a solution of an electrolyte containing the relevant cation (Y) which is to be exchanged with exchangeable cations (X) in the clay:



This reaction proceeds to equilibrium, the extent of which depends upon the nature of the ions X and Y, their relative concentrations, the nature of the clay and on any secondary reactions. In the present invention, the multivalent cation employed is more strongly adsorbed by the clay than the exchangeable alkali metal cations of the clay (which, as has already been stated, will normally be sodium cations) and this means that the equilibrium position of the exchange reaction lies well to the right hand side. Examples of suitable multivalent cations are the alkaline earth metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) as well as other multivalent metal cations such as Al^{3+} . Other multivalent cations which should be considered as within the scope of this invention are Fe^{3+} , Cr^{3+} , Tl^{4+} , Zn^{2+} and Pb^{2+} . Thus, in a cation exchange process to be employed in the present invention, the kaolinitic clay to be treated is contacted in aqueous suspension with an electrolyte containing a multivalent metal cation, the cation preferably being chosen from one of those referred to above. It is within the scope of the invention to contact the clay in aqueous suspension with two or more electrolytes so that two or more different cations are present in solution. The solution should of course be free from salts having monovalent cations. The aqueous solution containing an electrolyte may be formed by dissolving in water a water-soluble salt having a multivalent cation. Good results may be achieved by employing preferably at least 0.1% and preferably no more than 5% by weight, based on the weight of dry clay, of the water-soluble salt.

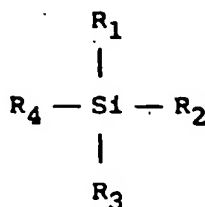
[0015] As a result of the treatment of the kaolinitic clay (either by washing or a cation exchange operation) the amount of exchangeable alkali metal cations as a proportion of the total exchangeable alkali metal cations in the clay mineral decreases significantly, although the actual magnitude of change can vary considerably between different clays having different characteristics and different initial concentrations of exchangeable alkali metal cations. For the purposes of the present invention, it is necessary that the exchangeable alkali metal cation content should be reduced to 750 ppm or less.

[0016] The kaolinitic clay is hydrous before treatment since any calcination would render the cations unexchangeable. After treatment, the kaolinitic clay is preferably calcined to a calcined kaolinitic clay (or metakaolin), at a temperature, for example, of at least 500°C for a time which, according to the method used for calcination, may range from a fraction of a second to 10 hours. The temperature and duration of calcination should not be such that the calcined kaolinitic clay undergoes further reactions to form a significant proportion of crystalline compounds; as such, the temperature of calcination should not normally exceed about 1250°C.

[0017] The particle size distribution of the starting kaolinitic clay is not presently believed to be important.

[0018] The kaolinitic clay for incorporation in the elastomeric composition, whether in a calcined or uncalcined state,

may advantageously be surface treated with at least 0.05% by weight, and preferably at least 0.25% by weight, but generally not more than 5% by weight, based on the weight of dry treated kaolinitic clay, of a substituted silane having the general formula:-



where

R_1 is an aminoalkyl group, a mercaptoalkyl group or an alkenyl group, for example vinyl or allyl, or an alkyl group having from 1 to 20 carbon atoms;

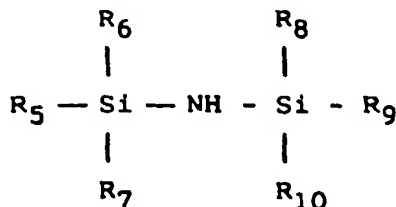
R_2 is a hydroxy group, a halogen atom, a hydroxyalkyl group or an alkoxy group; and

R_3 and R_4 (which may be the same or different) are each hydrogen, halogen atom, an alkyl group, a hydroxyalkyl group or an alkoxy group.

[0019] In radicals R_2 , R_3 and R_4 the alkyl, hydroxyalkyl and alkoxy groups preferably have from 1 to 4 carbon atoms. Halogen is defined as fluorine, chlorine, bromine or iodine.

[0020] The treated kaolinitic clay may, alternatively (or in addition), be surface treated with a similar quantity to that of the silane with:

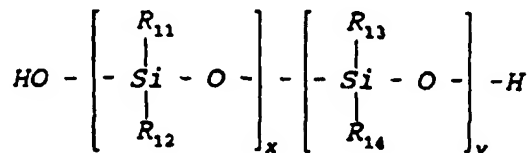
(a) a silazane of the general formula



in which R_5 and R_9 (which may be the same or different) are each an alkenyl group, for example vinyl or allyl, or an alkyl group having from 1 to 4 carbon atoms; and

R_6 , R_7 , R_8 and R_{10} (which may be the same or different) are each hydrogen or an alkyl group having from 1 to 4 carbon atoms; or

(b) a polysiloxane of general formula



where R_{13} is hydrogen, an alkyl group having from 1 to 4 carbon atoms or an alkenyl group, e.g. vinyl or allyl and R_{11} , R_{12} , and R_{14} (which may be the same or different) are each hydrogen or an alkyl group having from 1 to 4 atoms;

y is from 1 to 50% of $(x+y)$;

and $x+y$ is from 2 to 200; or

c) an organically substituted zirconate, titanate or zircoaluminate.

[0021] The kaolinitic clay may be combined directly with an elastomer in, for instance, a particulate or granular form. Other conventional adjuvants may be introduced directly into the mix of clay and elastomer or, alternatively, may be introduced as a component of granules of the elastomer. The composition, including the mineral filler, may be formed into articles by, for example, moulding or extruding. Thus, the composition may be extruded to form a length of an electrically insulating layer on an electric cable.

[0022] The elastomer may be natural rubber or a synthetic rubber such as a homopolymer or a copolymer of ethylene and/or propylene, or a thermoplastic elastomer; the specific elastomer to be used in the present invention will depend on the requirements of the final product.

[0023] The kaolinitic clay may be, for example, a kaolin clay or alternatively a ball clay having at least 60% by weight kaolinite content.

[0024] According to a second aspect of the present invention, there is provided a process for preparing an elastomeric composition incorporating a kaolinitic clay mineral filler, which process comprises:

providing a kaolinitic clay mineral which (a) is a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 or (b) is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral having a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm and a content of exchangeable alkali metal cations not exceeding 750 ppm; and

combining the kaolinitic clay mineral with an elastomeric material to form a resultant elastomeric composition.

[0025] In accordance with a third aspect of the present invention, there is provided a particulate kaolinitic clay filler which (a) is a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 ppm or (b) is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm and a content of exchangeable alkali metal cations not exceeding 750 ppm; for use as a mineral filler in elastomeric cable insulation.

[0026] In accordance with a fourth aspect of the present invention, there is provided elastomeric cable insulation containing a mineral filler, characterised in that said mineral filler is a particulate kaolinitic clay filler which (a) is a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm and a content of exchangeable alkali metal cations not exceeding 750 ppm or (b) is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 ppm. The elastomeric cable insulation of this aspect of the invention should exhibit a dissipation factor ($\tan \delta$) which is less than 0.003.

EXAMPLE 1

[0027] Samples of calcined kaolinitic clay were prepared by calcining the following raw kaolinitic clays:-

Clay A: A kaolin clay from Devon, England having a particle size distribution such that 29% by weight consisted of particles having an equivalent spherical diameter larger than 10 μm and 41% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μm .

Clay B: A kaolin clay from Georgia, U.S.A. having a particle size distribution such that 1% by weight consisted of particles having an equivalent spherical diameter larger than 5 μm and 94% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μm .

Clay C: A kaolin clay from Georgia, U.S.A. having a particle size distribution such that 4% by weight consisted of particles having an equivalent spherical diameter larger than 10 μm and 56% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μm .

Clay D: A ball clay from Devon, England having a particle size distribution such that 7% by weight consisted of particles having an equivalent spherical diameter larger than 5 μm and 77% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μm .

[0028] A 200g sample of each of the above clays was mixed with 800ml of distilled water by means of a low shear, laboratory paddle mixer. Calcium chloride dihydrate was added as a powder in the amount of 1% by weight of the dihydrate, based on the weight of dry clay, with continued stirring. The resultant suspension was stirred continuously for 30 minutes after which it was filtered and the filter cake dried for 16 hours at 80°C and pulverised in a pestle and mortar.

[0029] Each sample of calcium treated clay was calcined in a silica tray loaded to a depth of about 15mm in a

laboratory muffle furnace at a temperature of 1100°C for 1 hour. After this time the trays were removed and the calcined clay allowed to cool in the air.

[0030] A sample of each clay was also analysed for sodium, calcium and magnesium cations before and after treatment with calcium chloride by the following method. A 5g sample of each clay was weighed out into a 100ml conical flask. 50ml of a 1M solution of ammonium acetate was transferred by pipette into the flask and the resulting slurry shaken to disperse the clay. The flask was left to stand for 16 hours and the suspension was then filtered by means of a stainless steel pressure filtration device fitted with a 0.45 micron membrane filter. The clarified solution was analysed for sodium, calcium and magnesium content by inductively coupled plasma (ICP) spectroscopy. A sample of each clay was also analysed for non-exchangeable potassium ions by an X-ray fluorescence technique and the results were expressed in terms of parts by weight of potassium ion per million parts by weight of clay.

[0031] EPDM rubber compositions of the type suitable for electric cable insulation were prepared according to the following formulation:-

Ingredient	Parts by weight
EPDM	100
low density polyethylene	5
paraffin wax	5
zinc oxide	5
90% red lead in rubber	6
antioxidant	1.5
dicumyl peroxide	2.6

[0032] In each case a master batch of the above formulation was prepared on a laboratory twin roll mill heated to 70-80°C. 62.5g portions of the master batch of rubber, 30g of one of the calcined kaolinitic clay samples and 0.5g of vinyl triethoxysilane were then mixed together on the twin roll mill heated to 70°C. The rubber composition was removed from the mill in sheet form and transferred to a preheated mould of dimensions 150mm x 150mm x 2mm. The composition was placed between sheets of cellulose film and cured in a laboratory hydraulic press with steel plates at 17.2 MPa (2500 psi) and 170°C for 20 minutes. The moulded sheet was cooled in air and its thickness measured by means of a micrometer. In each case a test piece was cut from the sheet having the shape of a major circular segment of radius 50mm and chord length 90mm adjacent to an isosceles triangle of base 90mm and sides 65mm. The test piece was aged in air for 2 days at 90°C to drive off volatile by-products of the curing process.

[0033] The value of the dissipation factor ($\tan \delta$) was measured for each test piece by placing the test piece in a test cell between two circular aluminium electrodes which were loaded together by means of a small hydraulic press at a pressure of 0.4 MPa. The temperature in the test cell was maintained at 90°C. One electrode was connected to earth and the other electrode to a 500 volts, 50Hz A.C. supply. The test cell was connected in one arm of a Schering Bridge manufactured by Teltex AG of Switzerland and the value of $\tan \delta$ was determined directly by balancing the bridge.

[0034] The results obtained are set forth in Table I below:

Table I

	Cations (ppm)				$\tan \delta$
	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	
Clay A untreated	67	150	116	26,553	0.0083
Clay A treated	18	430	18	26,553	0.0060
Clay B untreated	1138	208	24	166	0.0042
Clay B treated	24	888	20	166	0.0020
Clay C untreated	1855	107	18	1328	0.0074
Clay C treated	414	1972	12	1328	0.0021
Clay D untreated	876	448	140	6638	0.0039
Clay D treated	214	1976	32	6638	0.0029.
Note "ppm" means parts by weight per million parts by weight of dry clay.					

EXAMPLE 2

[0035] Samples of calcined kaolinitic clay were prepared by calcining the following raw kaolinitic clays:-

- 5 Clay E: A kaolin clay from Spain having a particle size distribution such that 2% by weight consisted of particles having an equivalent spherical diameter larger than 10 μ m and 65% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μ m.
- Clay F: A kaolin clay from Spain having a particle size distribution such that 0.05% by weight consisted of particles having an equivalent spherical diameter larger than 10 μ m and 80% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μ m.
- 10 Clay G: A kaolin clay from Georgia, U.S.A. having a particle size distribution such that 0.05% by weight consisted of particles having an equivalent spherical diameter larger than 10 μ m and 80% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μ m.
- Clay H: A kaolin clay from Georgia, U.S.A. having a particle size distribution such that 0.02% by weight consisted of particles having an equivalent spherical diameter larger than 10 μ m and 93% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μ m.
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[0036] Clay E was prepared by passing the raw clay slurry through a trommel to separate coarse non-kaolinitic material and then subjecting the slurry containing solid material which consisted predominantly of kaolinitic clay to a particle size separation in hydraulic cyclones to produce a fine product having the particle size distribution already indicated. The suspension of the fine product from the hydrocyclones was then dewatered by filtration and the cake thermally dried. No reagents containing alkali metal cations were used during the preparation.

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[0037] Clay F was prepared in a similar manner to Clay E except that the fine product suspension from the hydraulic cyclones had a mean particle diameter of approximately 2 μ m. This suspension was then subjected to a further particle size separation step in a centrifuge to produce a suspension of a fine product having the particle size distribution already indicated. This fine product was the dewatered by filtration and the cake thermally dried. No reagents containing alkali metal cations were used during the preparation.

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[0038] Clays G and H had been prepared by beneficiation in suspension in water, using dispersing agents which were sodium salts, and the clays had been dewatered by spray drying.

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[0039] A sample of each of the clays was calcined in a laboratory muffle furnace at a temperature of 1100°C for 1 hour as described in Example 1. A sample of each clay was also analysed for exchangeable sodium, calcium and magnesium ions, and for non-exchangeable potassium ions, as described in Example 1.

[0040] Filled EPDM rubber compositions containing each of the samples of calcined clay were then prepared exactly as described in Example 1, and in each case the value of the dissipation factor ($\tan \delta$) was measured.

35 **[0041]** The results obtained are set forth in Table II below:

	Cations (ppm)				$\tan \delta$
	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	
40 Clay E (invention)	4149	30	1160	136	0.0022
Clay F (invention)	5145	30	312	68	0.0023
Clay G (comparative)	2157	1060	135	26	0.0037
Clay H (comparative)	1328	820	168	24	0.0063

45 **[0042]** It can be seen from the above results that, when the EPDM rubber composition contains, as a filler, a calcined clay prepared from a kaolinitic clay which contains less than 10,000 ppm of non-exchangeable potassium ions and less than 750 ppm of exchangeable sodium ions, the dissipation factor ($\tan \delta$) is of the order of 0.002, which is an acceptable value. If, however, one or other of these requirements is not satisfied, the dissipation factor is of the order of 0.003 or above and the dielectric loss from a cable insulated with the EPDM composition would be unacceptable, especially at high voltages.

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Claims

- 55 1. An elastomeric composition including a kaolinitic clay mineral filler, characterised in that said kaolinitic clay mineral (a) is a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal

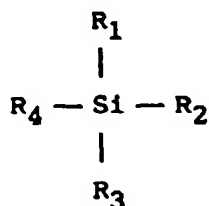
cations not exceeding 750 ppm or (b) is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral having a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm and a content of exchangeable alkali metal cations not exceeding 750 ppm.

- 5 2. An elastomeric composition according to claim 1, wherein said content of non-exchangeable alkali metal cations does not exceed 7,500 ppm.
3. An elastomeric composition according to claim 1 or 2, wherein said content of exchangeable alkali metal cations does not exceed 500 ppm.
- 10 4. An elastomeric composition according to claim 1, 2 or 3, wherein the kaolinitic clay is surface treated with at least 0.05% by weight based on the weight of dry treated kaolinitic clay, with:

(a) a substituted silane of the general formula

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where R_1 is an aminoalkyl group, a mercaptoalkyl group or an alkenyl group, for example vinyl or allyl, or an alkyl group having from 1 to 20 carbon atoms;

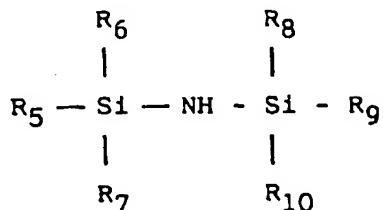
R_2 is a hydroxy group, a halogen atom, a hydroxyalkyl group or an alkoxy group; and

R_3 and R_4 (which may be the same or different) are each hydrogen, halogen atom, an alkyl group, a hydroxy-alkyl group or an alkoxy group.

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(b) a silazane of the general formula

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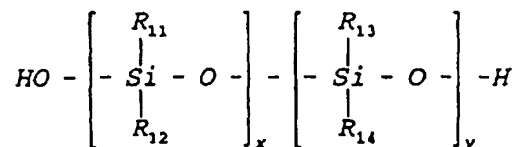
in which R_5 and R_9 (which may be the same or different) are each an alkenyl group, for example vinyl or allyl, or an alkyl group having from 1 to 4 carbon atoms; and

R_6 , R_7 , R_8 and R_{10} (which may be the same or different) are each hydrogen or an alkyl group having from 1 to 4 carbon atoms; or

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(c) a polysiloxane of general formula

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where R_{13} is hydrogen, an alkyl group having from 1 to 4 carbon atoms or an alkenyl group, e.g. vinyl or allyl and R_{11} , R_{12} , and R_{14} (which may be the same or different) are each hydrogen or an alkyl group having from 1 to 4 atoms;

y is from 1 to 50% of $(x+y)$;

and x+y is from 2 to 200; or
d) an organically substituted zirconate, titanate or zircoaluminate.

- 5 5. A process for preparing an elastomeric composition incorporating a kaolinitic clay mineral filler, which process comprises:
providing a kaolinitic clay mineral which (a) is a hydrous kaolinitic clay mineral which has a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 or (b) is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral having a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm and a content of exchangeable alkali metal cations not exceeding 750 ppm; and
10 combining the kaolinitic clay mineral with an elastomeric material to form a resultant elastomeric composition.
6. A process according to claim 5, wherein the kaolinitic clay mineral is prepared by (a) selecting a clay which naturally, or after beneficiation, has a content of non-exchangeable alkali metal cations below 10,000ppm, (b) treating the
15 clay, either during beneficiation or in a separate step if necessary, such that the resultant treated clay has an exchangeable alkali metal cations content not exceeding 750 ppm and (c) if necessary, calcining the treated kaolinitic clay mineral.
7. A process according to claim 6, wherein the kaolinitic clay is treated in step (b) by subjecting the kaolinitic clay to a cationic exchange operation whereby exchangeable alkali metal cations in the clay are removed and replaced by multivalent cations or by subjecting an aqueous suspension of the beneficiated clay to filtration whereby ex-
20 changeable alkali metal cations are removed in solution
8. A process according to claim 7, wherein the kaolinitic clay is subjected to a cationic exchange operation in which it is contacted in aqueous suspension with an electrolyte containing a multivalent metal cation.
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9. The use as a mineral filler in elastomeric cable insulation, of a particulate kaolinitic clay filler (a) which is a hydrous kaolinitic clay mineral having a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 ppm or (b) is a calcined kaolinitic clay mineral prepared by calcining a hydrous kaolinitic clay mineral having
30 a content of non-exchangeable alkali metal cations not exceeding 10,000 ppm (parts by weight per million parts by weight of dry clay) and a content of exchangeable alkali metal cations not exceeding 750 ppm.
10. Elastomeric cable insulation prepared from an elastomeric composition as claimed in any one of claims 1 to 4.
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11. Elastomeric cable insulation according to claim 10 having a dissipation factor ($\tan \delta$) of less than 0.003, wherein the dissipation factor is the tangent of the loss of angle, δ , by which the phase difference between applied voltage and resulting current deviates from 90°.
- 40 12. Elastomeric cable insulation prepared from an elastomeric composition comprising, as a filler, a kaolinitic clay mineral which has been treated to reduce significantly the number of monovalent exchangeable cations, said cable insulation having a reduced dissipation factor when compared with the same cable insulation including as the filler the untreated kaolinitic clay mineral.

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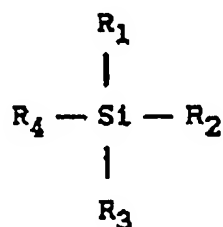
Patentansprüche

1. Elastomere Zusammensetzung, umfassend einen Kaolinit-Tonmineral-Füllstoff, der dadurch gekennzeichnet ist, dass das Kaolinit-Tonmineral (a) ein wasserhaltiges Kaolinit-Tonmineral ist, das nicht mehr als 10000 ppm (Gew.-
50 Teile pro Million Gew.-Teile wasserfreier Ton) nicht-austauschbare Alkalimetallkationen und nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält, oder (b) ein kalziniertes Kaolinit-Tonmineral ist, das hergestellt wird durch Kalzinieren eines wasserhaltigen Kaolinit-Tonminerals, das nicht mehr als 10000 ppm nicht-austauschbare Alkalimetallkationen und nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält.
- 55 2. Elastomere Zusammensetzung nach Anspruch 1, deren Gehalt an nicht-austauschbaren Alkalimetallkationen nicht höher als 7500 ppm liegt.
3. Elastomere Zusammensetzung nach Anspruch 1 oder 2, deren Gehalt an austauschbaren Alkalimetallkationen

nicht höher als 500 ppm liegt.

4. Elastomere Zusammensetzung nach Anspruch 1, 2 oder 3, wobei der Kaolinit-Ton oberflächenbehandelt ist mit mindestens 0,05 Gew.%, bezogen auf das Gewicht des wasserfreien behandelten Kaolinit-Tons, von:

(a) einem substituierten Silan der allgemeinen Formel:

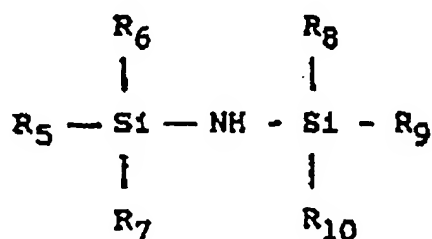


wobei R_1 ein Aminoalkyl-, ein Mercaptoalkyl- oder ein Alkenylrest, bspw. Vinyl oder Allyl, oder ein Alkylrest mit 1 bis 20 Kohlenstoffatomen ist;

R_2 eine Hydroxylgruppe, ein Halogenatom, ein Hydroxyalkylrest oder ein Alkoxyrest ist; und

R_3 und R_4 (die gleich oder verschieden voneinander sein können) jeweils ein Wasserstoffatom, ein Halogenatom, ein Alkylrest, ein Hydroxyalkylrest oder ein Alkoxyrest sind;

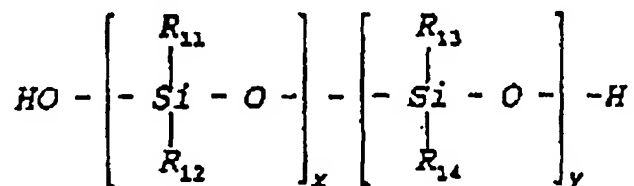
(b) einem Silazan der allgemeinen Formel:



wobei R_5 und R_9 (die gleich oder verschieden voneinander sein können) jeweils ein Alkenylrest, bspw. Vinyl oder Allyl, oder ein Alkylrest mit 1 bis 4 Kohlenstoffatomen sind; und

R_6 , R_7 , R_8 und R_{10} (die gleich oder verschieden voneinander sein können) jeweils ein Wasserstoffatom oder ein Alkylrest mit 1 bis 4 Kohlenstoffatomen sind; oder

(c) einem Polysiloxan der allgemeinen Formel



wobei R_{13} ein Wasserstoffatom, ein Alkylrest mit 1 bis 4 Kohlenstoffatomen oder ein Alkenylrest, bspw. Vinyl oder Allyl, ist, und R_{11} , R_{12} und R_{14} (die gleich oder verschieden voneinander sein können) jeweils ein Wasserstoffatom oder ein Alkylrest mit 1 bis 4 Kohlenstoffatomen sind;
 y 1 bis 50% von $(x + y)$ ausmacht;
 und $x + y$ von 2 bis 200 reicht; oder
 (d) einem organisch substituierten Zirkonat, Titanat oder Zirkoaluminat.

5. Verfahren zur Herstellung einer elastomeren Zusammensetzung mit einem Kaolinit-Tonmineral-Füllstoff, umfassend:

Bereitstellen eines Kaolinit-Tonminerals, welches (a) ein wasserhaltiges Kaolinit-Tonmineral ist, das nicht mehr als 10000 ppm (Gew.-Teile pro Million Gew.-Teile wasserfreier Ton) nicht-austauschbare Alkalimetallkationen und nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält, oder (b) ein kalziniertes Kaolinit-Tonmineral ist, das hergestellt wird durch Kalzinieren eines wasserhaltigen Kaolinit-Tonminerals, das nicht mehr als 10000 ppm nicht-austauschbare Alkalimetallkationen und nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält; und

Vermengen des Kaolinit-Tonminerals mit einem elastomeren Material, so dass man daraus eine elastomere Zusammensetzung erhält.

6. Verfahren nach Anspruch 5, wobei das Kaolinit-Tonmineral hergestellt wird durch

(a) Auswählen eines Tons, der natürlicherweise oder nach Aufbereitung weniger als 10000 ppm nicht-austauschbare Alkalimetallkationen enthält,
 (b) Behandeln des Tons, entweder während der Aufbereitung oder - sofern nötig - in einem gesonderten Schritt, so dass der resultierende behandelte Ton nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält, und
 (c) falls erforderlich, Kalzinieren des behandelten Kaolinit-Tonminerals.

7. Verfahren nach Anspruch 6, wobei der Kaolinit-Ton in Schritt (b) behandelt wird, indem er einem Kationenaustausch-Vorgang unterworfen wird, wodurch die austauschbaren Alkalimetallkationen im Ton entfernt werden und durch mehrwertige Kationen ersetzt werden, oder indem eine wässrige Suspension des aufbereiteten Tons filtriert wird, wodurch austauschbare Alkalimetallkationen in Lösung entfernt werden.

8. Verfahren nach Anspruch 7, wobei der Kaolinit-Ton bei einem Kationenaustauschvorgang in einer wässrigen Suspension mit einem Elektrolyten zusammengebracht wird, der ein mehrwertiges Metallkation enthält.

9. Verwendung als Mineralfüllstoff in einer elastomeren Kabelisolierung von einem teilchenförmigen Kaolinit-Ton-Füllstoff, der (a) ein wasserhaltiges Kaolinit-Tonmineral ist, das nicht mehr als 10000 ppm (Gew.-Teile pro Million Gew.-Teile wasserfreier Ton) nicht-austauschbare Alkalimetallkationen und nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält, oder (b) ein kalziniertes Kaolinit-Tonmineral ist, das hergestellt wird durch Kalzinieren eines wasserhaltigen Kaolinit-Tonminerals, das nicht mehr als 10000 ppm (Gew.-Teile pro Million Gew.-Teile wasserfreier Ton) nicht-austauschbare Alkalimetallkationen und nicht mehr als 750 ppm austauschbare Alkalimetallkationen enthält.

10. Elastomere Kabelisolierung, hergestellt aus einer elastomeren Zusammensetzung nach einem der Ansprüche 1 bis 4.

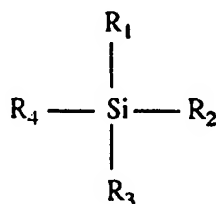
11. Elastomere Kabelisolierung nach Anspruch 10 mit einem Verlustfaktor ($\tan \delta$) unter 0,003, wobei der Verlustfaktor der Tangens des Verlustwinkels δ ist, wodurch die Phasendifferenz zwischen angelegter Spannung und resultierendem Strom von 90° abweicht.

12. Elastomere Kabelisolierung, hergestellt aus einer elastomeren Zusammensetzung, umfassend als Füllstoff ein Kaolinit-Tonmineral, das so behandelt ist, dass die Anzahl einwertiger austauschbarer Kationen erheblich geringer ist, wobei die Kabelisolierung gegenüber der gleichen Kabelisolierung mit unbehandeltem Kaolinit-Tonmineral als Füllstoff einen geringeren Verlustfaktor aufweist.

Revendications

1. Composition élastomère renfermant une charge à base d'un minéral argileux kaolinitique, caractérisée en ce que ledit minéral argileux kaolinitique (a) est un minéral argileux kaolinitique hydraté qui a une teneur en cations métalliques alcalins non échangeables ne dépassant pas 10000 ppm (parties en poids par million de parties en poids d'argile sèche) et une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm ou (b) est un minéral argileux kaolinitique calciné préparé par calcination d'un minéral argileux kaolinitique hydraté ayant une teneur en cations métalliques alcalins non échangeables ne dépassant pas 10000 ppm et une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm.
2. Composition élastomère selon la revendication 1, dans laquelle ladite teneur en cations métalliques alcalins non échangeables ne dépasse pas 7500 ppm.
3. Composition élastomère selon la revendication 1 ou 2, dans laquelle ladite teneur en cations métalliques alcalins échangeables ne dépasse pas 500 ppm.
4. Composition élastomère selon la revendication 1, 2 ou 3, dans laquelle l'argile kaolinitique est traitée en surface avec au moins 0,05% en poids rapporté au poids de l'argile kaolinitique traitée sèche, de

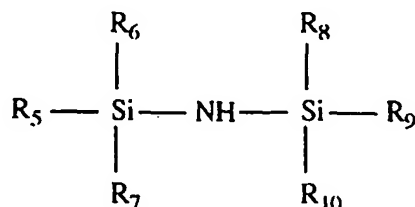
(a) un silane substitué ayant pour formule générale



dans laquelle R_1 est un groupe aminoalkyle, un groupe mercaptoalkyle ou un groupe alcényle, par exemple vinyle ou allyle, ou un groupe alkyle ayant de 1 à 20 atomes de carbone;

R_2 est un groupe hydroxy, un atome d'halogène, un groupe hydroxyalkyle ou un groupe alcoxy; et R_3 et R_4 (qui peuvent être identiques ou différents) sont chacun un atome d'hydrogène, un atome d'halogène, un groupe alkyle, un groupe hydroxyalkyle ou un groupe alcoxy;

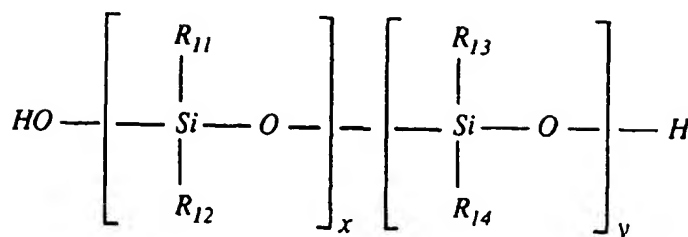
(b) un silazane de formule générale



dans laquelle R_5 et R_9 (qui peuvent être identiques ou différents) sont chacun un groupe alcényle, par exemple vinyle ou allyle, ou un groupe alkyle ayant de 1 à 4 atomes de carbone; et

R_6 , R_7 , R_8 et R_{10} (qui peuvent être identiques ou différents) sont chacun un atome d'hydrogène ou un groupe alkyle ayant de 1 à 4 atomes de carbone; ou

(c) un polysiloxane de formule générale



dans laquelle R_{13} est un atome d'hydrogène, un groupe alkyle ayant de 1 à 4 atomes de carbone ou un groupe alcényle, par exemple vinyle ou allyle, et R_{11} , R_{12} , et R_{14} (qui peuvent être identiques ou différents) sont chacun un atome d'hydrogène ou un groupe alkyle ayant de 1 à 4 atomes de carbone;

y vaut de 1 à 50% de (x+y);

et x+y vaut de 2 à 200; ou

(d) un zirconate, un titanate ou un zircoaluminate, à substituant organique.

5. Procédé de préparation d'une composition élastomère renfermant une charge à base d'un minéral argileux kaolinitique, ledit procédé comprenant les étapes consistant :

à fournir un minéral argileux kaolinitique qui (a) est un minéral argileux kaolinitique hydraté qui a une teneur en cations métalliques alcalins non échangeables ne dépassant pas 10000 ppm (parties en poids par million de parties en poids d'argile sèche) et une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm ou (b) est un minéral argileux kaolinitique calciné préparé par calcination d'un minéral argileux kaolinitique hydraté ayant une teneur en cations métalliques alcalins non échangeables ne dépassant pas 10000 ppm et une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm; et

à combiner le minéral argileux kaolinitique avec un matériau élastomère pour former une composition élastomère résultante.

6. Procédé selon la revendication 5, dans lequel le minéral argileux kaolinitique est préparé par (a) sélection d'une argile qui, naturellement ou après enrichissement, a une teneur en cations métalliques alcalins non échangeables en dessous de 10000 ppm, (b) traitement de l'argile, soit pendant l'enrichissement soit dans une étape distincte si nécessaire, de telle sorte que l'argile traitée résultante ait une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm et (c) si nécessaire, calcination du minéral argileux kaolinitique traité.

7. Procédé selon la revendication 6, dans lequel on traite l'argile kaolinitique dans l'étape (b) en soumettant l'argile kaolinitique à une opération d'échange cationique, ce par quoi les cations métalliques alcalins échangeables présents dans l'argile sont éliminés et remplacés par des cations polyvalents, ou en soumettant une suspension aqueuse de l'argile enrichie à une filtration, ce par quoi les cations métalliques alcalins échangeables sont remis en solution.

8. Procédé selon la revendication 7, dans lequel l'argile kaolinitique est soumise à une opération d'échange cationique au cours de laquelle elle est mise en contact en suspension aqueuse avec un électrolyte contenant un cation métallique polyvalent.

9. Utilisation comme charge minérale dans un revêtement isolant élastomère pour câble, d'une charge de type argile kaolinitique particulière (a) qui est un minéral argileux kaolinitique hydraté ayant une teneur en cations métalliques alcalins non échangeables ne dépassant pas 10000 ppm (parties en poids par million de parties en poids d'argile sèche) et une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm ou (b) qui est un minéral argileux kaolinitique calciné préparé par calcination d'un minéral argileux kaolinitique hydraté ayant une teneur en cations métalliques alcalins non échangeables ne dépassant pas 10000 ppm (parties en poids par million de parties en poids d'argile sèche) et une teneur en cations métalliques alcalins échangeables ne dépassant pas 750 ppm.

10. Revêtement isolant élastomère pour câble préparé à partir d'une composition élastomère selon l'une quelconque des revendications 1 à 4.

11. Revêtement isolant élastomère pour câble selon la revendication 10 ayant un facteur de dissipation ($\tan \delta$) inférieur

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à 0,003, où le facteur de dissipation est la tangente de l'angle de perte, δ , qui fait que le déphasage entre la tension appliquée et le courant qui en résulte s'écarte de 90° .

- 5 12. Revêtement isolant élastomère pour câble préparé à partir d'une composition élastomère comprenant, en guise de charge, un minéral argileux kaolinitique qui a été traité de façon à diminuer significativement le nombre de cations échangeables monovalents, ledit revêtement isolant pour câble ayant un facteur de dissipation diminué par comparaison au même revêtement isolant pour câble renfermant en guise de charge le minéral argileux kaolinitique non traité.

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